

OST TECHNICAL PROGRESS REPORT TEAM WORK PLAN--FY 2001 RESULTS

TITLE: C₁ Chemistry Team

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DESCRIPTION: The C₁ Chemistry Team supports the programs of several NETL Product Teams and the Ultra-Clean Fuels Focus Area by conducting exploratory research on catalytic methods for the conversion of single-carbon compounds into liquid fuels and/or chemicals

RESEARCH OBJECTIVES: The research goals and objectives of the C₁ Chemistry Team are to investigate specific aspects of the advanced technologies for the production of ultra-clean fuels. Specific research involves developing data to model solubility of gases in Fischer-Tropsch waxes, reducing the cost of syngas production by novel catalysts, developing a process that will use a liquid hydrocarbon fuel as the hydrogen source in an on-board fuel cell, developing an understanding of hydrocarbon chain growth on carbon supported cobalt and cobalt/platinum catalysts, developing methods for the direct conversion of methane (either alone or within methane hydrates) to liquid hydrocarbons, and developing an understanding of the properties of methane hydrates in their natural environment. Passenger transportation vehicles in the future may be powered by a fuel cell. These vehicles will employ an onboard reformer that will use a liquid hydrocarbon fuel to produce the hydrogen necessary for powering the fuel cell. Current reforming technologies produce carbon monoxide (CO) as a byproduct of the reforming process. Carbon monoxide acts as a poison upon contact with the proton exchange membrane (PEM) fuel cell (Pt-based) catalyst. Our goal is to develop a process that will use a liquid hydrocarbon fuel as the hydrogen source in an on-board fuel cell without the production of CO.

LONG TERM GOALS / RELATIONSHIP TO NETL'S PRODUCT LINE(S): It has been estimated that the world's supply of natural gas will be sufficient to meet the demand well into the next century. Lately, most of the near-term projected use of natural gas is for replacement of other fossil fuels in the generation of electricity. However, the supplies of natural gas can also be used for conversion to chemicals and transportation fuels. A prime example of this is on the north slope of Alaska. An efficient and competitive process for conversion of the natural gas reserves could add an extra 20-30 years of life to the trans-Alaskan pipeline. At present, the most probable scenario for the conversion of the natural gas, in remote areas such as Alaska, is by partial oxidation of the methane by an ion-transport membrane reactor to produce syngas, followed by Fischer-Tropsch technology to produce liquids. The C₁ Chemistry Team focuses its research efforts on the conversion of natural gas into chemicals and fuels. This is accomplished by researching several different reaction pathways, broken down into multiple tasks.

Syngas is a valuable feedstock for producing transportation fuels (specifically high quality diesel fuel from Fischer-Tropsch (FT) processes), hydrogen, fuel additives, and other chemicals. Since production of syngas and FT processes are carried out catalytically, the development of new and novel catalysts is very important for utilization of natural gas, particularly for producing liquid fuels. The Downstream Gas Processing Product Team is working with other DOE agencies in developing a method for the production of clean diesel fuels, such as those produced by FT.

Methane hydrates have the potential of being a major energy resource. To date, little research has been conducted on the conversion of the methane while it is still contained within the hydrate. The photocatalytic conversion project will attempt to address this. If successful, the photocatalytic conversion will be able to convert the methane in the hydrate *in situ*, eliminating the need to mine the hydrate or displace the methane and convert it in a separate process.

Any of these processes would, if successful, reduce U.S. dependence on foreign supplies of transportation fuels and allow for utilization of remote gas fields, such as those located on the north slope of Alaska.

SUMMARY ACCOMPLISHMENTS: In the area of technology transfer in FY01, the C1 Chemistry Team made 5 poster and 8 oral presentations of their research accomplishments at national meetings, published 6 non-refereed articles and 1 refereed article, had 2 additional refereed articles accepted for publication, submitted 1 article for refereed publication, issued 1 U.S. patent, and filed another U.S. patent application. These are detailed in Appendix A.

Photocatalytic Conversion of Methane Hydrates

The Natural Gas Processing Product Team funded this project in FY01. The high-pressure view cell was modified through experience gained in FY00 and now is able to reproducibly form hydrates. Methane hydrates were formed from both methane and double-distilled water and from methane and simulated seawater inside the view cell. The formation and dissociation of methane hydrates was investigated on samples formed under varying methane head pressures. The addition of a surfactant to the water prior to formation of hydrates increased methane uptake by the hydrate to >98% of the theoretical limit.

The hydrates were prepared containing two different photocatalysts and exposed to a full spectrum from a high-pressure mercury vapor lamp. Products of reaction included methanol, hydrogen, ethane, carbon dioxide and oxygen. Photoconversion was also conducted on the pure hydrates formed in double-distilled and simulated seawater. A “memory effect” observed during the formation of hydrates was investigated.

Summary of accomplishments for the methane hydrates project: 1 U.S. patent issued, 1 U.S. patent filed, 4 presentations given, and 1 refereed-paper published.

Robust FT Catalyst Development

A key problem limits use of iron FT catalysts in slurry-phase reactors: maintaining attrition-resistance (and thus particle size) of the relatively inactive small iron catalyst particles at conditions needed for sufficient activity. Iron-based FT catalysts also undergo attrition due to crystallographic changes during the FT reaction. The iron is converted from a carbide to an oxide and back to a carbide form during the reaction. If the catalyst could be contained within a cage (either organic or inorganic) such that the reactants and products can enter and leave while still containing the catalyst particles, the lifetime of an FT reaction could be extended.

Research on the robust catalyst was halted in the first quarter of FY01 due to the inability to procure the necessary equipment needed to complete the investigation.

Dry Reforming of Methane

This project was initiated to develop and test new and commercial catalysts for the conversion of methane to syngas. The task for FY01 was to further develop a series of nickel-based catalysts by reducing the deposition of carbon onto the catalyst. These catalysts have been tested for more than 330 hours at atmospheric pressure and a temperature range of 750 to 850°C with no sign of deactivation.

High-pressure tests on dry reforming catalysts (Pt/ZrO₂ & Pt/CeZrO_x) were completed. This research was a collaborative effort with Dr. Daniel Resasco of the University of Oklahoma.

Carbon deposition on noble metal catalysts was investigated using ¹³C labeled methane. These catalysts are used for the CO₂ reforming of methane.

Summary of accomplishments for the dry reforming of methane project: A book chapter entitled "Effect of Pressure on Catalyst Activity and Carbon Deposition During CO₂ Reforming of Methane over Noble-Metal Catalysts" was accepted for publication by Kluwer Academic/Plenum Publisher; a book chapter is in press on "Methane Dry Reforming Over Carbide, Nickel-Based, and Noble Metal Catalysts", an ACS book edited by Dr. Chunshan Song of PSU (2001); a presentation at the 2001 Spring National Meeting of the American Chemical Society National Meeting; and a presentation at the 2001 Spring National Meeting of the AIChE Meeting.

Reforming of Hydrocarbons

This research was funded in FY01 under the Ultra-Clean Fuels Focus Area. The objective of this research is to reduce the quantity of carbon monoxide (CO) produced during hydrocarbon reforming to near-zero levels. During FY01 catalysts were synthesized, and reforming experiments were conducted with these catalysts.

Summary of accomplishments for the reforming of hydrocarbons project: 2 non-refereed papers

published; a presentation at the 2001 Spring National Meeting of the American Chemical Society; and a presentation at the 2001 Fall National Meeting of the American Chemical Society.

RESULTS:

Photocatalytic Conversion of Methane Hydrates

Research in FY01 focused on perfecting the synthesis of methane hydrates and the photocatalytic conversion of the methane contained within the hydrate molecule.

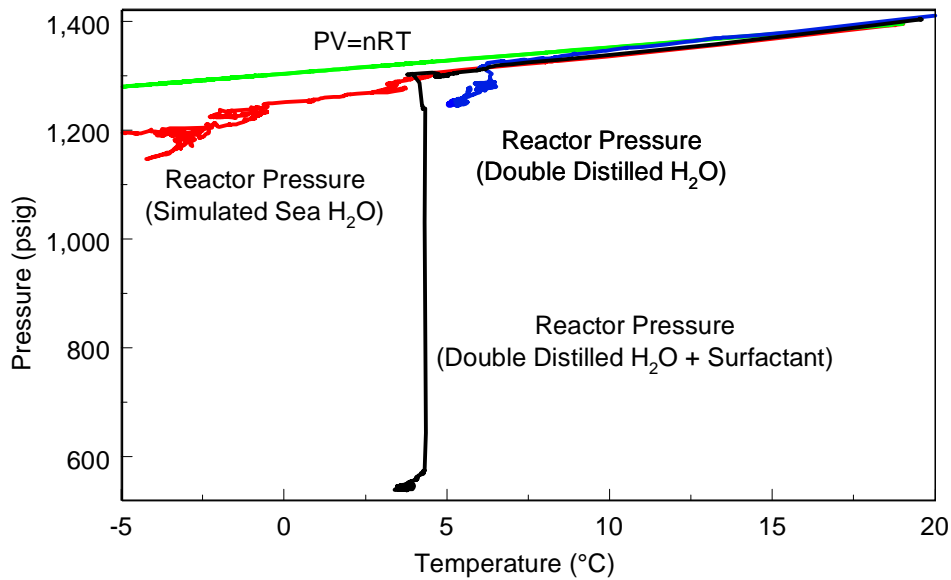
Methane hydrates are clathrates that exist in the form of a methane-water ice-like crystalline material and which occur naturally in deep-ocean and permafrost areas. Methane hydrates form naturally at ocean depths between ~280 meters (920 feet) and 4,000 meters (13,125 feet) when the water temperature is between 0°C (at 280 meters) and 23°C (at 4,000 meters) and water pressures are between 600 psi (at 280 meters) and 6,000 psi (at 4000 meters). It has been estimated that more organic carbon is contained within methane hydrates than all other forms of fossil fuels combined.

The photocatalytic process involves exposing methane hydrates formed in the laboratory at NETL to a full spectrum light source. The light causes electrons in the semiconductor photocatalyst to be promoted from a filled electron level below the forbidden band to the conduction band. Once in the conduction band, the electron is available for reaction. The electron is picked up by an electron transfer agent that reacts with the water in the hydrate molecule to produce a hydroxyl radical. The hydroxyl radical can then react with the molecule of methane contained within the hydrate molecule, producing a methyl radical. The methyl radical reacts with a second water molecule producing methanol and hydrogen.

During FY01, methane hydrates were produced in the laboratory that contained the theoretical limit of methane. This was accomplished by modifying the synthesis and through addition of a surfactant to the water. Methane concentrations increased dramatically from <40% methane uptake to >98%.

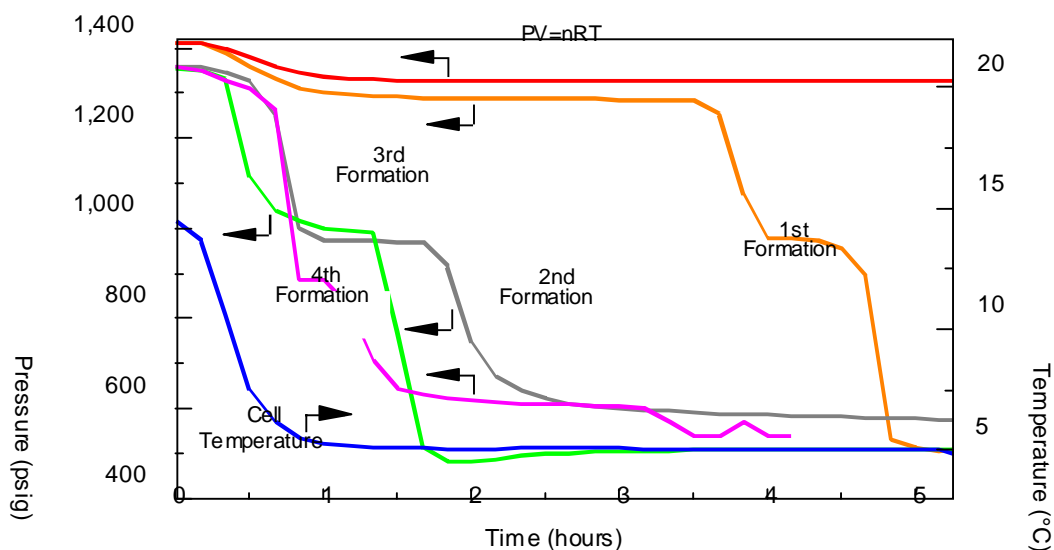
Two photocatalysts were tested for their ability to convert methane contained within the hydrate molecule to methanol and hydrogen. These were a promoted tungsten oxide and a titanium oxide catalyst. Both catalysts converted the methane contained within the hydrate molecule with the production of methanol, hydrogen, ethane, and other oxidation products, such as carbon dioxide and formic acid.

PRESSURE-TEMPERATURE PROFILE OF HYDRATE FORMATION



The “memory effect” observed during the formation of hydrates was investigated. It was observed in our laboratory that if a hydrate is formed, dissociated, and reformed, the reforming occurs faster than the initial formation. The presence of this effect is due to microscopic hydrate molecules still present in solution even though it appears (both visually and by the pressure of methane in the cell returning to pre-hydrate levels) that the hydrate is completely dissociated. These microscopic hydrate molecules act as seeds for the formation of larger hydrate molecules. The effect can be negated by warming the solution to a higher temperature (in this example $>18^{\circ}\text{C}$), thereby dissociating all of the hydrate molecules.

MULTIPLE HYDRATE FORMATIONS



Robust FT Catalyst Development

A literature survey was conducted to determine a cage starting material. Two were selected for study, furfuryl alcohol that is pyrolyzed and a commercial (partially polymerized) polyfurfuryl resin. The alcohol and resin were procured. A sample of NETL prepared iron-FT catalyst, which has been extensively studied, was selected for encapsulation. Laboratory space and equipment for preparation of the robust catalyst has been obtained. Research on the robust catalyst was halted in the first quarter of FY01 due to the inability to procure the necessary equipment needed to complete the investigation.

Dry Reforming of Methane

The objective of the dry reforming of methane research is to develop and test new and novel catalysts for the cost-effective production of synthesis gas and to further the understanding of reforming reactions. The main challenge is in developing catalysts that operate at lower steam/carbon, oxygen/carbon, and CO_2 /carbon ratios without the formation of excess carbon.

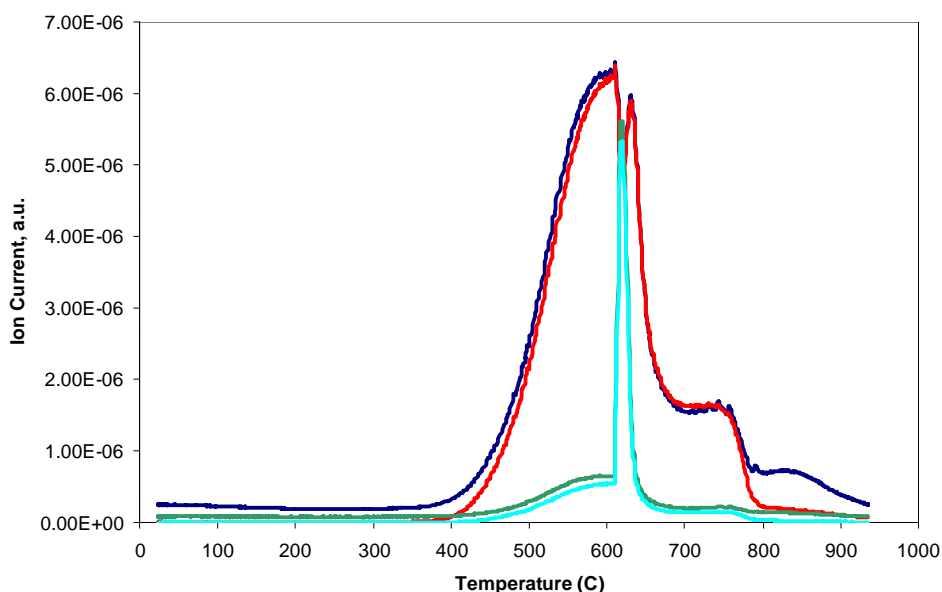
The conversion of hydrocarbons to hydrogen and syngas will play an important role in the 21st century ranging from large gas-to-liquid plants and hydrogen plants for refineries to small units providing hydrogen for fuel cells. Syngas-based routes are efficient, but still expensive; 60% of the capital investment in a gas-to-liquids plant is for syngas generation. The key issue in improving catalyst performance is to avoid the formation of carbon on the catalyst

Reducing carbon formation requires a multi-faceted approach: a better understanding of reforming reactions; using more expensive noble metal catalysts, such as ruthenium and rhodium; increasing the oxygen content of the support; using supports such as CaO and MgO or a combination of both; and decreasing the rate of carbon formation by addition of alkali metals such as Li, Na, K, and Cs.

The task for FY01 was to further develop a series of nickel-based catalysts by reducing the deposition of carbon on to the catalyst. These catalysts have been tested for more than 330 hours at atmospheric pressure and a temperature range of 750 to 850°C with no sign of deactivation.

High-pressure tests on dry reforming catalysts (Pt/ZrO₂ & Pt/CeZrO_x) were completed. This research was a collaborative effort with Dr. Daniel Resasco of the University of Oklahoma.

**TPO of carbon deposited on Ni/La₂O₃ reacted at 800°C, 14atm,
¹³CH₄/CO₂ = 1:1, 20cc/min for 10min.**



Carbon deposition on noble metal catalysts was investigated using ¹³C labeled methane. Catalysts of this type are used for the reforming of methane with CO₂. Temperature-programmed oxidation (TPO) was used to characterize the catalysts after reforming reactions and to elucidate reaction mechanisms. These characterizations identified that both methane and carbon dioxide contribute to carbon deposition. Addition of alkali and alkaline-earth metals significantly reduced carbon formation on these catalysts.

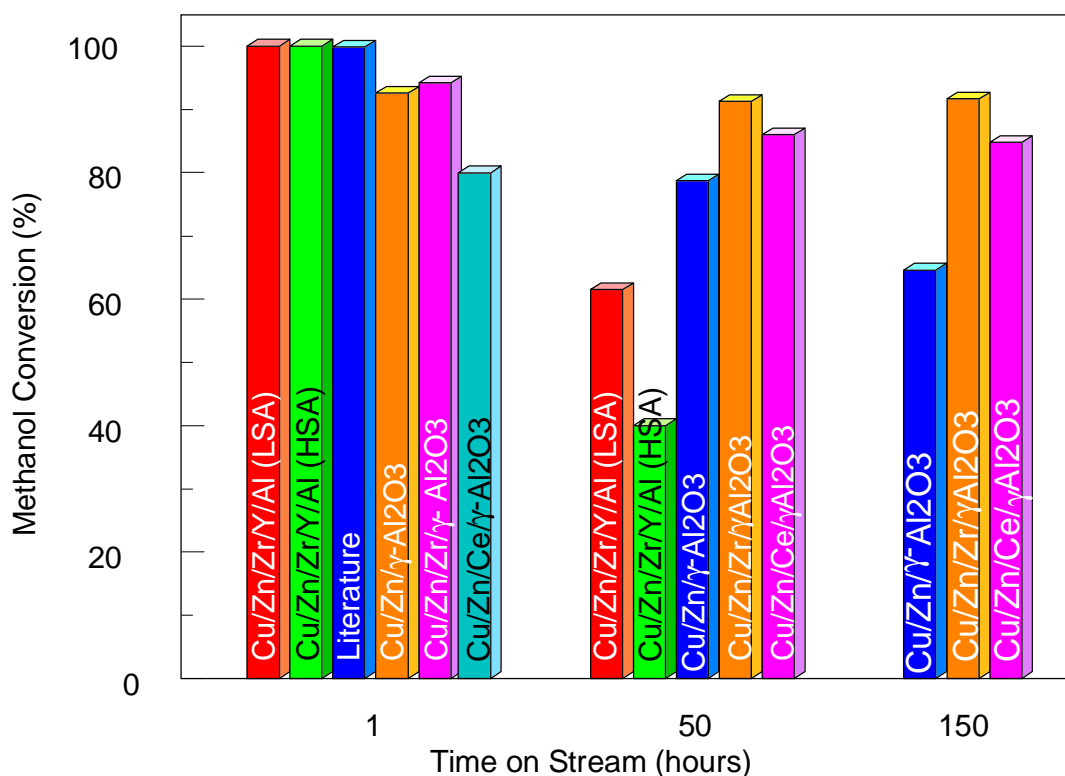
A book chapter entitled "Effect of Pressure on Catalyst Activity and Carbon Deposition During CO₂ Reforming of Methane over Noble-metal Catalysts" was accepted for publication by Kluwer Academic/Plenum Publisher. A book chapter is in press on "Methane Dry Reforming Over Carbide, Nickel-Based, and Noble Metal Catalysts", an ACS book, edited by Dr. Chunshan Song of PSU

(2001). A presentation was made at the 2001 Spring National Meeting of the American Chemical Society National Meeting. A presentation was also made at the 2001 Spring National Meeting of the AIChE Meeting.

Reforming of Hydrocarbons

This research was funded in FY-2000 under the Ultra-Clean Fuels Focus Area. The objective of this research is to reduce the quantity of carbon monoxide (CO) produced during hydrocarbon reforming to near-zero levels. Current investigations favor methanol as the liquid hydrocarbon for fuel cells and the chemical carrier for hydrogen. The reasons are due to its ready availability and its high energy density, which allows for easier storage and transportation. To eliminate the CO poisoning of the PEM fuel cell, a catalyst must be developed which operates at moderate temperatures (330-400 °C) and whose main products will be hydrogen and carbon dioxide. Most reforming processes require high temperatures and will produce a large CO yield. High operating temperatures are not cost effective or considered safe by the public for on-board fuel cells.

CATALYST STABILITY AS FUNCTION OF SURFACE AREA



Research during FY01 was designed to advance the development of novel catalysts for the reforming of methanol. The work included conducting an extensive literature survey to determine what research had been conducted to date. After the literature survey, an appropriate catalyst was

selected and synthesized at NETL. Five samples of the reforming catalyst were tested without the addition of steam to the reactant stream. Results from this investigation show that the catalyst developed at NETL performs as well as the catalysts reported in the literature which incorporate steam in the feed.

A paper was presented in the Hydrogen Symposium at the 2001 Spring National Meeting of the American Chemical Society, and a second paper was presented in the Fuel for Fuel Cells Symposium at the 2001 Fall National Meeting of the American Chemical Society. A refereed publication: "Hydrogen Production from the Reforming of Liquid Hydrocarbons" was submitted to Catalysis Today in August 2001.

DISCLAIMER: Reference in this report to any specific commercial product, process, or service is to facilitate understanding and does not necessarily imply its endorsement by the United States Department of Energy.

ACKNOWLEDGMENTS: The Ultra-Clean Fuels Focus Area and the Downstream Natural Gas Processing Product Team sponsored research conducted by the C1 Chemistry Team.
NETL Contact: Charles E. Taylor

Appendix A

Award:

Edward P. Ladner, a physical science technician with the C₁ Chemistry Team, was named the 2001 Technician of the Year by the American Chemical Society's Western Pennsylvania Technician Affiliate Group.

Presentations: 5 Poster, 8 Oral

NATCat2000 Title: Photocatalyst for the Production of Methanol from Methane and Water Using Visible Light. October 12-13, 2000, Argonne, IL.

NATCat2000 Title: In-situ Filtration of F-T Wax. October. 12, 2000, Argonne, IL.

2001 Gordon Research Conference on Hydrocarbon Fuels. Title: "National Energy Technology Laboratory's Ultra-Clean Fuels Focus Area". January 7-11, 2001, Ventura, CA.

INEEL National Laboratory Hydrate Conference. Title: "NETL Methane Hydrate Overview". January 24-25, 2001, Salt Lake City, UT.

221st ACS National Meeting. Title: "Reduction Of CO₂ In Steam Using a Photocatalytic Process To Form Formic Acid". April 1-5, 2001, San Diego, CA.

221st ACS National Meeting. Title: "Carbon Deposition on Methane Dry Reforming Catalysts at

Higher Pressures". April 1-5, 2001, San Diego, CA.

221st ACS National Meeting. Title: "Catalyst Development for Hydrogen Production from the Reforming of Liquid Hydrocarbons". April 1-5, 2001, San Diego, CA.

28th Annual NOBCCChE National Conference. Title: "National Energy Technology Laboratory's Ultra-Clean Fuels Focus Area". April 8-14, 2001, Baltimore, MD.

6th Natural Gas Conversion Symposium. Title: "Novel Techniques for the Conversion of Methane Hydrates". June 17-22, 2001, Gridwood, AK.

222nd ACS National Meeting. Title: "NETL's Ultra-Clean Fuels Focus Area: an Overview", August 19-23, 2001, Chicago, IL.

222nd ACS National Meeting. Title: "Effect of Pressure on the Carbon Deposition Route in CO₂ Reforming of ¹³CH₄ on Nobel Metal Catalysts". August 19-23, 2001, Chicago, IL.

222nd ACS National Meeting. Title: "Hydrogen Production from the Reforming of Liquid Hydrocarbons". August 19-23, 2001, Chicago, IL.

222nd ACS National Meeting. Title: "Effect of Pressure on the Carbon Deposition Route in CO₂ Reforming of ¹³CH₄ on Nobel Metal Catalysts" August 20, 2001, Chicago, IL.

Publications: 6 Non-Refereed, 5 Refereed (2 Submitted, 2 Accepted, 1 Published)

Manns, C. R. and Taylor, C. E. (2001). Catalyst development for hydrogen production from the reforming of liquid hydrocarbons. Preprints of the Fuel Division of the ACS, 46(1), p. 6.

Link, D. D. and Taylor, C. E. (2001). Reduction of CO₂ in steam using a photocatalytic process to form formic acid. Preprints of the Fuel Division of the ACS, 46(1), p. 284.

Shamsi, A. (2001). Carbon deposition on methane dry reforming catalysts at higher pressures. Preprints of the Fuel Division of the ACS, 46(1), p. 94.

Taylor, C. E. and Manns, C. R. (2001). Hydrogen production from the reforming of liquid hydrocarbons. Preprints of the Fuel Division of the ACS, 46(2), p.652.

Taylor, C. E. and Cugini, A. V. (2001). NETL's Ultra-Clean Fuels Focus Area: An overview. Preprints of the Fuel Division of the ACS, 46(2), p. 402.

Shamsi, A. and Johnson, C. D. (2001). Effect of pressure on the carbon deposition route in CO₂ reforming of ¹³CH₄ on noble metal catalysts. Preprints of the Fuel Division of the ACS, 46(2), p. 410.

Link, D. L., Taylor, C. E., and Ladner, E. P. (2001). Novel techniques for the conversion of methane hydrates. Studies in Surface Science and Catalysis, 136, pp. 543-548.

(2001). Methane dry reforming over carbide, nickel-based, and noble metal catalysts. CO₂ Conversion and Utilization in Refinery and Chemical Processing. ?: Kluwer Academic/ Plenum Publishers.

(2001). Reduction of CO₂ in steam using a photocatalytic process to form formic acid. CO₂ Conversion and Utilization in Refinery and Chemical Processing. ?: Kluwer Academic/ Plenum Publishers.

Manns, C. R., Howard, B. H., and Taylor, C. E. (submitted, 2001). Hydrogen production from the reforming of liquid hydrocarbons. Catalysis Today.

U.S. Patents: 1 Granted, 1 Filed.

Mass spectrometer capillary inlet system for low flow reactors. October 1999. Approved by the NETL Patent Board for submission to the U.S. Patent Office, February 2000, Patent application submitted to the U.S. Patent Office in September 2001.

Process for the photoconversion of methane hydrates. U.S. Patent 6,267,849, July 31, 2001. A patent describing the process for the production of methanol and hydrogen from methane hydrates utilizing visible light and a semi-conductor catalyst.